

Development of precious metal-free electrocatalysts based on carbon nanocomposites for anion-exchange membrane fuel cell cathode

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Hydrogen plays a pivotal role as an energy carrier and especially in sustainable transportation, where low-temperature polymer electrolyte membrane fuel cells can be used. While proton-exchange membrane fuel cells are already commercialised, their widespread usage is hindered by the need of costly and scarce precious metal catalysts. Anion-exchange membrane fuel cell (AEMFC) could be feasible alternative as alkaline media allows to use cheaper catalyst materials. For instance, the Pt-based catalysts for oxygen reduction reaction (ORR) can be replaced with transition metal and nitrogen doped nanocarbons (M-N-C) in AEMFC. In developing efficient M-N-C catalysts, both the choice of transition metals and nanocarbon materials play important role as they are responsible for active site formation and efficient mass transport, respectively.^{1,2}

Herein, the ORR and AEMFC results are presented, where graphene and carbon nanotube (Gra/CNT) composite is doped with nitrogen and iron, cobalt or both of them via high-temperature pyrolysis.¹ All three catalyst materials exhibit high ORR activity in the rotating ring-disk electrode testing, however, the peroxide production during the ORR depends on the metal additive employed. Significant influence of the transition metal additive is evident from the AEMFC tests as bimetallic CoFe-N-Gra/CNT material shows superior performance as cathode electrocatalyst by reaching a maximum power density of 638 mW cm⁻². In addition, the M-N-Gra/CNT materials perform better in AEMFC than our previous investigations with just graphene as a support have shown, thus indicating that by combining nanocarbons, more beneficial structure is obtained.¹ We further continued to study the effect of carbon support and possible benefit of combining nanocarbons. As base nanocarbon, we synthesised ordered mesoporous carbon (OMC) using a simple soft-templating route.² To study the effect of porous structure of carbon support, the OMC (pore diameter ca. 7 nm) is mixed with highly microporous carbide-derived carbon (CDC) or carbon nanotubes (CNTs). The nanocarbon support is doped with nitrogen and both cobalt and iron via high-temperature pyrolysis. Three prepared catalysts, CoFe-N-OMC, CoFe-N-OMC/CDC and CoFe-N-OMC/CNT contained ca. 4 wt% nitrogen and 0.5 wt% of Co and 0.5 wt% of Fe with the metals being atomically dispersed as M-N_x type ORR-active sites. All three catalyst materials show the same and high electrocatalytic activity for ORR in 0.1 M KOH ($E_{1/2} = 0.84$ V vs RHE). The effect of porous structure of the catalysts is observed in AEMFC testing as the highest peak power density of 336 mW cm⁻² is reached with CoFe-N-OMC/CNT cathode material, which has both smaller (ca. 7 nm) and larger (15-40 nm) mesopores. Lower AEMFC performance is obtained with CoFe-N-OMC and micro-mesoporous CoFe-N-OMC/CDC catalyst materials.² These result also indicate that the preparation of novel nanocarbon composites helps to obtain suitable structure that is beneficial in the AEMFC application.

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References

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